

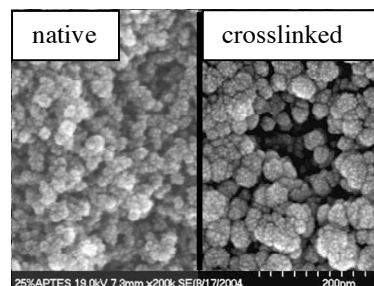
# Polymer Crosslinked 3-D Assemblies of Nanoparticles: Mechanically Strong Lightweight Porous Materials

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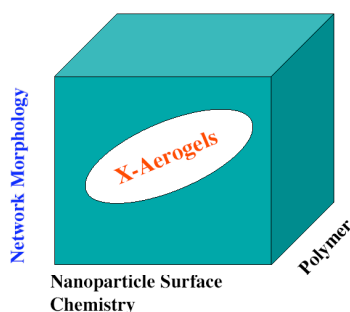
In analogy to supramolecular assemblies, which are pursued because of properties above and beyond those of the individual molecules, self-standing monolithic three-dimensional assemblies of nanoparticles also have unique properties attributed to their structure. For example, ultra low-density 3-D assemblies of silica nanoparticles, known as silica aerogels, are characterized by large internal void space, high surface area and very low thermal conductivity. Aerogels, however, are also extremely *fragile materials*, limiting their application to a few specialized environments, e.g., in nuclear reactors as Cerenkov radiation detectors, in space (refer to NASA's Stardust Program) and aboard certain planetary vehicles (thermal insulators on Mars Rovers in 1997 and 2004).

The fragility problem is traced to well-defined weak points in the aerogel skeletal framework, the interparticle necks. Using the surface functionality of the nanoparticle building blocks as a focal point, we have directed attachment of a conformal polymer coating over the entire framework, rendering all necks wider. Thus, although the bulk density may increase only by 3 $\times$ , the mesoporosity (pores in the range 2-50 nm) remains unchanged (Fig. 1), while the strength of the material increases by up to 300 $\times$ . Having addressed the fragility problem, aerogels are now robust materials, and a variety of applications, ranging from thermal/acoustic insulators to catalyst supports, to platform for sensors, and dielectrics are all within reach.



**Fig. 1.** SEMs of a native and of a polyurea crosslinked silica aerogel

Our approach employs molecular science to manipulate nanoscopic matter for achieving useful macroscopic properties, and in our view it resides at the core of what defines nanotechnology. In that spirit, this technology is expandable in three directions (Fig. 2). Thus, we have already crosslinked successfully amine-modified silica, and we anticipate that more rich chemistry will be realized by being creative with the nanoparticle



**Fig. 2.** The design space of X-aerogels

surface modifiers. On the other hand, although we do not expect orders-of-magnitude increase in strength, nevertheless, by varying the polymer we expect to impart other properties such as hydrophobicity, thermal stability and perhaps electrical conductivity. Besides polymers, crosslinkers will include metals and ceramics (e.g., through POSS precursors). Finally, network morphology directs load dissipation, and of  $\sim 30$  different crosslinked oxide aerogels, vanadia, whose structure is fibrous rather than particulate, yields a much stronger (by 4 $\times$ ) material than silica of the same density. It seems imperative to implement control of network morphology, even through templating.